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NEW POLYTETRAHYDROFURAN GRAFT COPOLYMERS

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Our discovery that tetrahydrofuran polymerization can be initiated by trifluoromethanesulfonate esters formed <u>in situ</u> from reactive alkyl or polymeric halides and silver trifluoromethanesulfonate has led to this investigation of the synthesis and characterization of a group of novel graft copolymers with potentially interesting and technologically useful combinations of properties. The study has shown that the method is general for heterocycles that will polymerize by cationic ring opening		

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20. Abstract (continued)

polymerization and that a variety of salts can be substituted for the silver trifluoromethanesulfonate. Properties of the first series of graft copolymers prepared in sufficient quantity for physical testing confirm the expectation that the behavior of the materials produced is related to the chemical structure of the backbone and of the branch, so that copolymers can be tailor-made for specific applications by proper choice of backbone and branch.

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STATEMENT OF PROBLEM

Our discovery that tetrahydrofuran polymerization can be initiated by trifluoromethanesulfonate esters formed in situ from reactive alkyl or polymeric halides and silver trifluoromethanesulfonate has led to this investigation of the synthesis and characterization of a group of novel graft copolymers with potentially interesting and technologically useful combinations of properties. The copolymers consist of hydrocarbon backbones with polyether branches randomly placed along the backbone. The objectives of this study were fourfold:

1. To determine what limitations exist with regard to choice of polymeric halide for backbone, of cyclic monomer for branches, and of metal salt for in situ generation of the active sites and subsequent growth of branches.
2. To find ways to characterize as fully as possible the resulting chemical structure of the products.
3. To exploit and optimize the most promising combinations of backbone, branch, and salt for the preparation of graft copolymers sufficient in amount for physical testing.
4. To study the physical properties of the graft copolymers prepared.

RESULTS AND CONCLUSIONS

The results of this study have been summarized in ten papers, in numerous presentations at technical meetings, and in progress reports to the U. S. Army Research Office. A list of the publications is attached. In the discussion which follows below, the numbers refer to the publications in which the relevant work is described in detail.

Scope of Halide, Heterocycle, and Salt

A variety of halides can be used but very reactive halides such as tertiary allylic halides or benzylic halides are preferred. This is not a severe limitation and graft copolymers have been prepared from eight backbones including poly(vinylchloride), styrene-vinylbenzylchloride copolymer, poly(chloroprene), chlorobutyl rubber, bromobutyl rubber, chlorinated EPDM, chlorinated poly(butadiene) and chlorinated butadiene styrene copolymer (1,9). Because of its high reactivity in these syntheses and its ready availability, poly(chloroprene) was selected as the backbone for initial detailed studies (2,3,6,8,9).

The mechanism by which growth of the polyether branches from the hydrocarbon backbone proceeds in these syntheses is cationic ring opening polymerization of the heterocycle. Therefore, any heterocycle which will produce polymer in this manner is suitable. Examples include tetrahydrofuran, 7-oxabicyclo[2.2.1]heptane, oxetane and substituted oxetanes, propylene oxide, styrene oxide, dioxolane, trioxane, thietane, and ϵ -caprolactone (1,2). Whenever "living" polymers can be prepared from the heterocycle (tetrahydrofuran, the

oxetanes, dioxolane), the resulting graft copolymers can be prepared pure, i.e., without unreacted backbone or homopolymer from the heterocycle. Because the polymerization of tetrahydrofuran is the most thoroughly studied cationic ring opening polymerization, tetrahydrofuran was selected as the heterocycle for initial detailed studies (3,4,6,7-9).

Many soluble metal salts with cations capable of stabilizing an onium ion polymerization (SO_3CF_3^+ , BF_4^+ , PF_6^+ , SbF_6^+ , ClO_4^+) can be used. Counterions such as PF_6^- and SbF_6^- lead to the highest polymerization rates and the most well-defined polymers. Silver salts are preferred but they are not ideal. The precipitated silver chloride formed as a byproduct of the initiation reaction is difficult to remove quantitatively. Even under the most favorable conditions discoloration and/or crosslinking of the isolated graft copolymer often occurs, possibly as a result of metallation of the backbone and later reactions of the silver (4-6,8). Preliminary studies with nitrosyl and nitryl hexafluorophosphates show promise of producing pure and soluble graft copolymers directly (9). With these salts the side products formed are gases, which are readily removed. Further study with these salts is desirable.

Characterization of the Chemical Structure of the Products

The products of the graft copolymerizations have been characterized by solubility, IR, NMR, GPC, osmometry and DTA (1-4,6,8,9). Pure graft copolymers are produced from combinations of backbones and heterocycles that are known to be stable under the reaction

conditions. With backbones such as bromobutyl rubber, which after dehalogenation is unstable with respect to conjugated dienes, the yields of graft copolymer are low. With poly(chloroprene) yields are high. With heterocycles (propylene oxide, styrene oxide, ϵ -caprolactone) that are known to undergo transfer and termination reactions during cationic propagation, the graft copolymers are contaminated by homopolymer.

Experimental determination of the number and length of the branches proved to be more difficult than anticipated. Degradation studies of poly(chloroprene)-poly(tetrahydrofuran) mixtures led to a new, rapid method of degrading poly(chloroprene), but some simultaneous degradation of the poly(tetrahydrofuran) was always suspected (10). Established methods of active center determination in poly(tetrahydrofuran) polymerizations all had disadvantages in our system, and finally a new method based on fluorescence spectroscopy was developed (7,8). This method showed that only 35% of the halogens predicted to be active from IR studies indeed lead to branches. The number of branches did not change in the course of the polymerization. Using this figure good agreement between predicted and experimental number average molecular weights of graft copolymers prepared using nitrosyl hexafluorophosphate was obtained (8,9).

Preparation of Graft Copolymers For Study of Physical Properties

A series of graft copolymers with poly(tetrahydrofuran) branches of varying molecular weight and with poly(chloroprene)

backbones were prepared readily in sufficient quantities for physical testing. Smaller quantities and with a lesser variety of molecular weights of the branches of graft copolymers from the same backbone but with branches from 7-oxabicyclo[2.2.1]heptane or dioxolane were also prepared.

Physical Properties of the Graft Copolymers

Tensile strength, work of adhesion, and dynamic mechanical analysis behavior of the graft copolymers was studied. The neoprene w-g-poly(tetrahydrofuran)'s were also studied by x-ray diffraction, and polarizing and transmission electron microscopy. Graft copolymers of poly(chloroprene) with flexible poly(tetrahydrofuran) branches show good physical properties that lie between those of the homopolymers from which they are derived. They behave like homogeneous materials and are especially promising as broad spectrum adhesives (3). Preliminary studies of graft copolymers with rigid branches from 7-oxabicyclo[2.2.1]heptane or dioxolane indicate phase separation and the graft copolymers show characteristics of both the backbone and the branch, although individual transitions are shifted. Graft copolymers from 7-oxabicyclo[2.2.1]heptane show promise for wide temperature applications (8). Further studies of physical properties are needed to properly evaluate these novel graft copolymers but this first study does indicate that this new method is a major step forward in tailor-making polymers with predictable combinations of properties.

PUBLICATIONS RESULTING FROM GRANT DAAG29-76-G-0118

1. P. Dreyfuss and J. P. Kennedy, J. Polym. Sci., Polym. Symp. 56, 129-13 (1977). "Alkyl Halides in Conjunction with Inorganic Salts for the Initiation of the Polymerization and Graft Copolymerization of Heterocycles."
2. P. Dreyfuss, T. Adaway, and J. P. Kennedy, J. Appl. Polym. Sci., Appl. Polym. Symp. 30, 183-192 (1977). "Polymerization and Grafting of Heterocyclic Monomers from Reactive Mono- and Macrohalides."
3. J. Lehmann and P. Dreyfuss, Adv. in Chem. (in press). "Effect of Branch Length of Neoprene-g-Poly(tetrahydrofuran) Copolymers on Properties." Also appeared in part in Polym. Preprints, 19, No. 1, 693-8 (1978).
4. Y. Eckstein and P. Dreyfuss, submitted to Macromolecules, "Polymerization and Graft Copolymerization of Tetrahydrofuran. I. Homopolymerization of Tetrahydrofuran in Presence of Perchlorate Salts and Organic Halides." Also appeared in part in Polym. Preprints 20, No. 1, 805-8 (1979).
5. P. Dreyfuss, submitted to Macromolecules, "Polymerization and Graft Copolymerization of Tetrahydrofuran. II. Comparison of Initiation Mechanism in Presence of Metal Perchlorates with Initiation Mechanism in Presence of Other Compounds."
6. Y. Eckstein and P. Dreyfuss, submitted to Macromolecules, "Polymerization and Graft Copolymerization of Tetrahydrofuran. III. Grafting of Polytetrahydrofuran from Neoprene W in the Presence of Perchlorate Salts." Also appeared in part in Polym. Preprints 20, No. 1, 805-8 (1979).
7. Y. Eckstein and P. Dreyfuss, submitted to Anal. Chem., "Rapid Quantitative Determination of Primary Amine Endgroups on Polymers Using Fluorescamine Reagent in Nonaqueous Solvents."
8. P. Dreyfuss, Y. Eckstein, D. P. Lee, and J. Lehmann, in Preparation for submission to Polym. Preprints for Washington ACS meeting, September, 1979 and later to J. Polym. Sci., "Comparison of the Properties of Neoprene with Flexible and Rigid Polyether Branches."
9. Y. Eckstein and P. Dreyfuss, in preparation for submission to J. Polym. Sci., "Nitrosyl and Nitryl Hexafluorophosphates in Initiation of Polymerization and Graft Copolymerization of Tetrahydrofuran."
10. J. Lehmann and P. Dreyfuss, to be prepared for submission to J. Polym. Sci., "A New, Rapid Method for Degrading Polychloroprene," previously described in progress report covering period from 31 December 1976 to 30 June 1977.

PERSONNEL SUPPORTED
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<u>Period</u>	<u>Name</u>	<u>% Calendar Year</u>
12/15/75 to 6/30/76	J. P. Kennedy	10
	P. Dreyfuss	50
	T. Adaway	b
7/1/76 to 12/31/76	J. P. Kennedy	10
	P. Dreyfuss	47
	K. Lee	16
	J. Lehmann	33
1/5/77 to 6/30/77	J. P. Kennedy	10
	P. Dreyfuss	41
	J. Lehmann	100
7/1/77 to 12/31/77	J. P. Kennedy	10
	P. Dreyfuss	50
	J. Lehmann	15
	R. A. Smith	c
1/1/78 to 6/30/78	J. P. Kennedy	5
	P. Dreyfuss	50
	D. P. Lee	33
	Y. Eckstein	16
	R. A. Smith	d
7/1/78 to 12/31/78	P. Dreyfuss	46
	Y. Eckstein	50
	D. P. Lee	16
1/1/79 to 1/31/79	Y. Eckstein	45

^a No degrees were granted. Personnel except T. Adaway and R. A. Smith were all Postdoctoral associates.

^b T. Adaway was paid \$200.

^c R. A. Smith was paid \$111.11/month for 3-1/2 months.

^d R. A. Smith was paid \$111.11/month for 6 months.